

# PATENT SPECIFICATION

(11) 1444 426

1444426

- (21) Application No. 48743/73 (22) Filed 19 Oct. 1973  
 (31) Convention Application No. 15473/72 (32) Filed 23 Oct. 1972 in (19)  
 (33) Switzerland (CH)  
 (44) Complete Specification published 28 July 1976  
 (51) INT CL<sup>2</sup> D06P 3/82 3/84 3/85  
 (52) Index at acceptance

D1B 2L10 2L13 2L14 2L17 2L18 2L19 2L1B 2L29A  
 2L29B 2L2A 2L32A 2L3 2L5D2 2L6 2L8 2T

(72) Inventors GEORG ROBERT and  
 GILBERT JOURNEAUX



## (54) DYEING PROCESS

(71) We, SANDOZ LTD., of Lichtstrasse 35, 4002 Basle, Switzerland, a Swiss Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for improving the dyeability to basic dyes of textile substrates comprising a basic dyeable component and a natural or synthetic polyamide component.

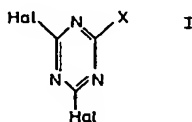
The difficulties encountered in dyeing or printing textile substrates comprising a dibasic dyeable component and a natural or synthetic polyamide component are well-known in the art. Thus, when such substrates are dyed or printed only with basic or cationic dyes, whilst the basic dyeable component is satisfactorily dyed, the polyamide component is not dyed in the true sense of the word but rather is soiled by the dye and this leads to poor fastness properties and the substrate having a so-called "skittery" appearance. This can to some extent be alleviated by employing a mixture of cationic and anionic dyes. However, again soiling of the polyamide component by the cationic dye component inevitably occurs, again resulting in unsatisfactory fastness properties. Further, mixtures of cationic and anionic dyes have the disadvantage that printing pastes comprising such a mixture generally have limited storage stability, reactions taking place leading to precipitations being formed therein.

The present invention provides a process for the dyeing or printing, using basic dyes, of textile substrates comprising a basic dyeable component and a natural or synthetic polyamide component, which process comprises, as a pretreatment step, applying the substrate a colourless compound having a) a polyamide fibre-reactive group and b) a carboxylic or sulphonic acid group and fixing the compound thereon, the substrate subsequently being dyed or printed with a basic dye.

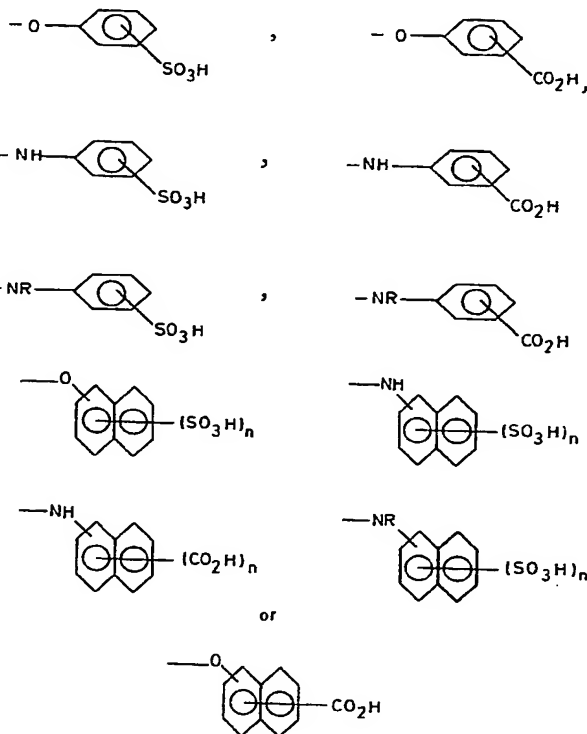
The compound having the fibre reactive group and the carboxylic or sulphonic acid group may be applied to the substrate in conventional manner, e.g. in liquor or paste form. The production and application of such liquor or paste may be carried out in analogous manner to as described in Swiss Patent 52 5997, which Patent also discloses colourless fibre reactive compounds eminently suitable for use in the present invention. Similarly, the fixation thereof on the substrate may be carried out in conventional manner for the fixation of fibre-reactive compounds, in dependence on the nature of the fibre reactive group carried by the compound. Fibre reactive groups are well documented in the literature along with methods of fixation thereof on polyamide substrates, e.g. by pH and temperature adjustments.

As examples of groups which may easily be made to react with a nitrogen atom of a polyamide may be given those containing reactive halogen atoms, particularly fluorine, chlorine or bromine atoms, such as halogen bearing triazinyl groups, particularly dihalogen triazinyl groups, trihalogen pyrimidyl groups, and carboxylic acid halide and sulphonic acid halide groups, and those containing carbon-carbon double bonds capable of addition.

As examples of said colourless compounds may be given compounds of formula I,



in which Hal signifies fluorine, chlorine or bromine, and  
X signifies a group of formula



in which R signifies an alkyl radical of 1 to 4 carbon atoms,  
n signifies 1, 2 or 3, and the aromatic nuclei are unsubstituted or further substituted by, e.g. 1 or 2, substituents selected from halogen, e.g. fluorine, chlorine or bromine, nitro, cyano or  $C_{1-4}$  alkyl or alkoxy groups.

In the compounds of formula I, the carboxylic acid or sulphononic acid groups are preferably in other than ortho-position to the oxa or imino linking groups.

The textile substrate to be dyed according to the present invention may, for example, be in yarn, woven, non-woven, knitted fleece or carpet form.

The basic dyeable component in the substrate may, for example, be basic dyeable polyacrylonitrile or basic dyeable polyester fibres, for example those containing sulphononic acid groups or carboxylic acid groups, e.g. as obtained when employing sulphophthalic acid in the production of polyester fibres.

As examples of natural polyamide components may be given wool, silk and leather, and, as examples of synthetic polyamide components may be given nylon 6, nylon 7, nylon 66, nylon 76 and nylon 610.

The application of the basic dye to the substrate may be carried out in conventional manner, e.g. using conventional dyeing liquors and printing pastes. As examples of basic dyes may be given those listed in Colour Index, Third Edition, Volume I, pages 1607 to 1688. The dye liquor or printing paste may be in the form of a coacervate system.

The dyeing liquors and printing pastes containing the basic dye may contain such auxiliary agents as are conventional in the art as well as acid dyes, disperse dyes and pigments. Further, the substrate may comprise components in addition to the basic dyeable component and natural or synthetic polyamide component. Thus, for example, it may contain polyester fibres dyeable with disperse dyes.

The invention is illustrated by the following Examples in which all parts and percentages are by weight and the temperatures in degrees Centigrade.

#### EXAMPLE 1

A knit fabric of a blend of modified polyacrylonitrile (containing sulphononic acid groups) fibre and wool (50:50) is pretreated in a bath. The pretreatment bath con-

ains 4% (by weight of goods) 2,4-dichloro-6-(phenylamino)-4'-sulphonic acid)-1,3,5-triazine. The pH value is adjusted to 4.5 with formic acid. The bath is then heated to 60°C, the fabric is immersed and kept in slight motion. The temperature is subsequently raised to 80°C and the treatment continued for an hour. The pH value is then adjusted to 9 by the addition of ammonia and the treatment is continued for another 20 minutes. The fabric is then rinsed in warm and cold water and dried. The material thus pretreated is printed with a printing paste of the following composition:

20 g C.I. Basic Violet 16  
Const. No. 48.013  
50 g Commercial thickener  
30 g benzyl alcohol  
2,5 g tartaric acid  
897,5 g water

The prints are then dried and fixed in steam at .5 kg/cm<sup>2</sup> pressure for 30 minutes. The fixed prints are rinsed in cold water, soaped at 50°C, rinsed again and dried. The prints obtained show a level dyeing of both the polyacrylonitrile and the wool component as well as good fastness properties.

#### EXAMPLE 2

A woven fabric of a blend of modified polyacrylonitrile (containing sulphonic acid groups) fibre and wool (40:60) is pretreated as in Example 1 and subsequently printed with a coacervate system printing paste. The printing paste is prepared as follows.

Using a propeller-type agitator,

10 parts nonyl phenyl pentaglycol ether and  
50 parts of a 30% aqueous solution of sodium ricinoleate and oleic acid  
sulphonate ester are stirred into  
500 parts thickening agent of 22% dextrin, 13% hydrolised starch and 65%  
water at room temperature on which two aqueous phases form according to  
the coacervation principle.  
5 parts tartaric acid 50% are added and then  
5 parts C.I. Basic Violet 16 and  
3 parts C.I. Acid Blue 23 entered in  
427 parts hot water and the resulting

1000 parts solution well stirred.

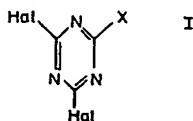
#### WHAT WE CLAIM IS:—

1. A process for the dyeing or printing, using basic dyes, of textile substrates comprising a basic dyeable component and a natural or synthetic polyamide component, which process comprises, as a pretreatment step, applying to the substrate a colourless compound having a) a polyamide fibre-reactive group and b) a carboxylic or sulphonic acid group, and fixing the compound thereon, the substrate subsequently being dyed or printed with a basic dye.

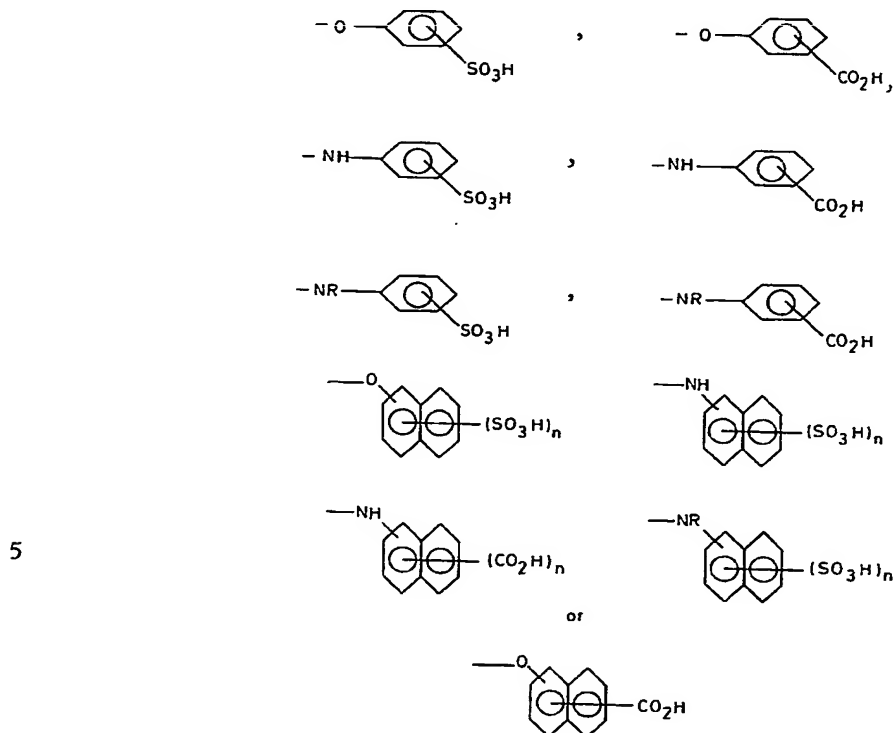
2. A process according to Claim 1, wherein the basic dyeable component is basic dyeable polyacrylonitrile or basic dyeable polyester fibres.

3. A process according to Claim 1 or Claim 2, wherein the natural or synthetic polyamide component is wool, silk, leather, nylon 6, nylon 7, nylon 66, nylon 76 or nylon 610.

4. A process according to Claim 1, 2 or 3, wherein the colourless fibre reactive compound is of formula I,



in which Hal signifies fluorine, chlorine or bromine, and  
X signifies a group of formula



in which R signifies an alkyl radical of 1 to 4 carbon atoms,  
 n signifies 1, 2 or 3, and the aromatic nuclei are unsubstituted or further substituted by substituents selected from halogen, nitro, cyano or  $C_{1-4}$  alkyl or alkoxy groups.

5. A process according to Claim 4, wherein, in the compounds of formula I, the aromatic nuclei are unsubstituted or further substituted by 1 or 2 substituents selected from halogen, nitro, cyano or  $C_{1-4}$  alkyl or alkoxy groups.

6. A process according to Claim 5, wherein, in the compounds of formula I, the aromatic nuclei are unsubstituted.

7. A process according to any one of the preceding Claims, wherein the substrate is in yarn, woven, non-woven, knitted, fleece or carpet form.

8. A process according to Claim 1, substantially as hereinbefore described with reference to either of the foregoing Examples.

9. A textile substrate, comprising a basic dyeable component and a natural or synthetic polyamide component, whenever dyed by a process according to any one of the preceding Claims.

B. A. YORKE & CO.,  
 Chartered Patent Agents,  
 98, The Centre,  
 Feltham,  
 Middlesex TW13 4EP.  
 Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1976.  
 Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.